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On the Evaluation of Surface Interactions by Inverse Gas Chromatography

Ulf Panzer[†] **and Henry P. Schreiber**[*]

Department of Chemical Engineering, Ecole Polytechnique, Box 6079, Stn. A,
Montreal, Quebec H3C 3A7, Canada

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ABSTRACT: This paper examines the applicability of inverse gas chromatography (IGC) to the quantification for polymer substrates of electron acceptor–donor (or Lewis acid–base) interactions. Polycarbonate is used as the reference stationary-phase material. Various options have been compared for the graphical representation of experimental data leading to the evaluation of acid–base contributions, and preference among these was accorded on the basis of the convenience and breadth of applicability. From the temperature dependence of these acid–base contributions, the enthalpies of acid–base interaction have been determined. These were found to correlate with donor and new acceptor numbers, both in thermodynamically consistent units. Parameters expressing the ability of the polycarbonate surface to accept or to donate electrons may now be compared on an unequivocal basis. The polymer may be described as being amphoteric but with predominant basicity.

Introduction

This paper is concerned with the application of inverse gas chromatography (IGC) for the evaluation of surface energies and interaction characteristics for polymers and other nonvolatile constituents of polymer systems. The subject gains importance with the continued increase in the use of multiphase composites and similar polymer formulations. The properties of these, of course, depend on the choice of starting materials but to a considerable degree also on the nature of the interfaces and interphases between these materials. Quantification of the latter constitutes a valuable objective of study.

Gas adsorption is a useful tool for gathering information on the chemical and thermodynamic state of solid surfaces. IGC has seen considerable evolution in this context.[1,2] Unlike conventional gas adsorption techniques, IGC measures adsorption down to extremely low gas or vapor concentrations, corresponding to nearly zero surface coverage. Adsorbate–adsorbent interactions are therefore the leading cause of adsorption effects. When no chemical bonds are involved, then thermodynamic functions such as the work of adhesion, W_A, between the components of a multiphase system are due to physical forces only. According to Fowkes,[3,4] W_A may be attributed to dispersion and to electron acceptor–donor (Lewis acid–base) interactions and written as

$$W_A = W_A^{\,D} + W_A^{\,ab} + W_A^{\,dipol} \qquad (1)$$

with $W_A^{dipol} \to 0$.

The use of IGC for the evaluation of acid–base properties of polymers, fibers, and fillers is currently much in vogue.[5–15] A number of theoretical and mathematical starting points exist for the derivation of expressions permitting the determination of these quantities. The principal objective of this paper is to compare the different methods for quantifying the contribution of electron acceptor–donor interactions from IGC data, using polycarbonate (PC) as the reference stationary phase. In addition, the acidity and basicity of PC is expressed in terms of acceptor and donor numbers which have common units (kcal/mol), permitting direct comparisons to be made between these surface interaction characteristics.

IGC and Thermodynamic Data

Gas adsorption chromatography rests upon the dependence of the retention volume of a volatile substance on its interaction energy with the stationary phase. In IGC the solid adsorbent to be characterized is the stationary phase, while known probe molecules are used as volatiles. In this paper we restrict our considerations to cases where only physical interactions take place and therefore where adsorption is reversible.

When the measurements are carried out at infinite dilution of the solutes or at zero surface coverage of the adsorbent and when adsorption is the dominant retention mechanism, then all thermodynamic parameters derived from V_N exclusively reflect the interaction between adsorbent and adsorbate.

The net retention volume V_N is given as

$$V_N = w_{corr}(t_r - t_0) \qquad (2)$$

where w_{corr} = corrected flow rate of carrier gas, t_r = retention time of the respective solute, and t_0 = retention time of the marker (air or methane). The free energy ΔG_A of adsorption per mole of solute is given by

$$\Delta G_A = -RT \ln V_N + \text{const} \qquad (3)$$

where R = gas constant, T = temperature, and the constant depends on the chosen reference state.[12,16,17] The analogy between the free energy of desorption $-\Delta G_A$ per mole of solute, and the work of adhesion W_A between the probe molecule and the solid, results in the equation

$$-\Delta G_A = NaW_A \qquad (4)$$

where N is Avogadro's number and a the surface area of an adsorbed probe molecule.

Dispersion and specific interactions are considered to contribute independently to the adsorption of probe molecules at the adsorbent surface. Hence, before considering the more general case of the adsorption of polar solutes, we begin with the adsorption of nonpolar solutes, capable only of dispersion interactions with the stationary phase. This may be exemplified by the adsorption of vapors such as the *n*-alkanes.

According to Fowkes,[18] the thermodynamic work of adhesion between some solid S and a liquid L, which only

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[*] Author to whom correspondence should be addressed.

[†] Permanent address: Institute of Polymer Research, Hohe Strasse 6, D-8010 Dresden, Germany.

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implicates dispersion interactions, is given by

$$W_A = W_A{}^D = 2(\gamma_S{}^D\gamma_L{}^D)^{1/2} \quad (5)$$

where the superscript D refers to dispersion components; thus, $\gamma_S{}^D$ and $\gamma_L{}^D$ are the dispersion components of the surface free energies of S and L, respectively.

Combining eqs 3–5 leads to

$$RT \ln V_N = 2N(\gamma_S{}^D)^{1/2}a(\gamma_L{}^D)^{1/2} + \text{const} \quad (6)$$

Therefore plotting $RT \ln V_N$ vs $a(\gamma_L{}^D)^{1/2}$ should give a straight line, from the slope of which the dispersion components of the solid surface free energy, $\gamma_S{}^D$, can be calculated. While $\gamma_L{}^D$ for *n*-alkanes is generally available (identical to the total surface free energy γ_L), the area *a* occupied by the adsorbed molecules may raise problems, given the possibility of different configurations at the adsorbent–adsorbate contact. There are various adsorption models differing in the assumed packing factors, but none take into account the possible dependence of the molecular area *a* on the forces exerted by the adsorbent.[19,20] Of course, it is possible to determine the molecular area experimentally, again by means of adsorption measurements, but these results also depend on the choice of adsorbing surface. In this work we used molecular areas as evaluated from IGC data by Schultz et al.[21] on neutral surfaces.

The applicability of eq 6 has been demonstrated for several polymer–vapor and filler–vapor systems.[7,12,13]

Specific Interactions. In the more general case of polar adsorbates, dispersion and specific interactions are capable of contributing independently to the total interaction between adsorbent and adsorbate and hence to the net retention volume V_N. An evaluation of the role and size of specific interactions requires a separation of the contributions from dispersion and nondispersion forces. As noted, the magnitude of dispersion effects is usually determined by using *n*-alkanes. If the adsorbent is capable of specific as well as of dispersion interactions, then the adsorption of polar solutes gives rise to an additional interaction term, leading to higher net retention volumes when compared with the occurrence of dispersion interactions alone. These additional interaction terms can be evaluated in a variety of ways:

(I) Using the thermodynamic considerations that led to eq 6 and plotting $RT \ln V_N$ vs $a(\gamma_L{}^D)^{1/2}$.

(II) Following the protocol of Papirer et al.[22,23] and plotting $\ln V_N$ versus the logarithm of the saturation vapor pressure of the solutes, $\log P_0$.

(III) As in Sawyer et al.,[24,25] by investigating the retention of hydrocarbons on modified silicas and separating dispersion and specific interactions by plotting the logarithm of retention volumes versus the boiling temperatures of the solutes, T_b.

Introduction of Lewis Acid–Base Concepts. Fowkes[3,4,26,27] applied the Lewis acid–base theory to problems in the field of surface chemistry and adhesion. When eq 1 is referred to, the acid–base contribution $W_A{}^{ab}$ to the work of adhesion can be determined from the change in enthalpy, $\Delta H_A{}^{ab}$, due to electron donor–acceptor interactions and the number of acid–base pairs.[4] This requires the introduction of concepts contained in theories of acid–base behavior. The two most frequently used theories are due to Drago and Gutmann.

Drago et al.[28,29] introduced the empirical, four-parameter equation

$$-\Delta H^{ab} = E_aE_b + C_aC_b \quad (7)$$

to predict the enthalpies ΔH_{ab} of formation of one-to-one molecular adducts in the gas phase and in poorly coordinating solvents. The *E* parameters are supposed to represent the electrostatic contributions to adduct stability, and the *C* parameters represent covalent contributions. Equation 7 was widely applied by Fowkes to surface chemistry in order to determine *E* and *C* parameters for solid surfaces and polymers.[4,27] According to the Drago concept, a molecule is either a Lewis acid or a Lewis base. This restriction is in conflict with the amphoteric character of most molecules, even when one functionality dominates.

According to the Gutmann acid–base concept,[30] a Lewis base is an electron pair donor (EPD) characterized by the donor number DN, and a Lewis acid is an electron pair acceptor (EPA) characterized by the acceptor number AN. The donor number DN is defined by Gutmann as the molar enthalpy of the reaction between the base and a reference acceptor, antimony pentachloride ($SbCl_5$), in a dilute solution of 1,2-dichloroethane.[31] Thus

$$\text{DN} = -\Delta H_{SbCl_5\text{-base}} \quad (8)$$

The acceptor numbers AN are defined as the relative ^{31}P NMR chemical shifts, $\Delta\delta$, induced in triethylphosphine oxide (Et_3PO) when it is dissolved in an acceptor solvent.[32] The AN values are arbitrarily scaled, by assigning a value of 0 to the shift induced by hexane and a value of 100 to the shift induced when antimony pentachloride is in a dilute solution of 1,2-dichloroethane.

Unlike Drago's *E&C* equation, this two-parameter model has the advantage of taking into account the coexistence in one chemical of both functionalities. This leads to the following expression for the enthalpy of a given acid–base pair:

$$-\Delta H_{ab} = \text{AN}_a\text{DN}_b \quad (9)$$

On the other hand, because of the arbitrary scaling of AN values and the asymmetry of AN and DN units, these descriptors of acidity and basicity are only related subjectively.

The problem of asymmetric AN and DN units can be circumvented empirically. For example, Deng and Schreiber[33] used eq 6 along with reference alkane, acid, and base probes for which values of the molecular area *a* were available, to determine empirical AN and DN data for polymer solids. These parameters were equated to the perpendicular distance from the reference line defined by alkane probes, of retention volumes for the acid and base probes. The resulting descriptors of the solid phase thus had units of *RT*. More sophisticated approaches are possible.

Recently, Riddle and Fowkes[34] have shown that the ^{31}P NMR shift $\Delta\delta$ of Et_3PO dissolved in acidic solvents is made up of two additive contributions: a dispersion contribution $\Delta\delta^d$ and a Lewis acid–base contribution $\Delta\delta^{ab}$. Consequently, AN values have to be corrected for this dispersion effect. In many cases, the correction is quite substantial. These authors have also found that the acid–base contributions $\Delta\delta^{ab}$ are directly proportional to the enthalpies of acid–base interaction between Et_3PO and acidic liquids. This results in new acceptor numbers AN*, having the same units as DN:

$$\text{AN*} = -\Delta H_{\text{acid-}Et_3PO} \quad (10)$$

Fowkes and Riddle further link AN* with the original AN numbers by the equation

$$\text{AN*} = 0.288(\text{AN} - \text{AN}^d) \quad (11)$$

where AN^d is the dispersion contribution reported by these

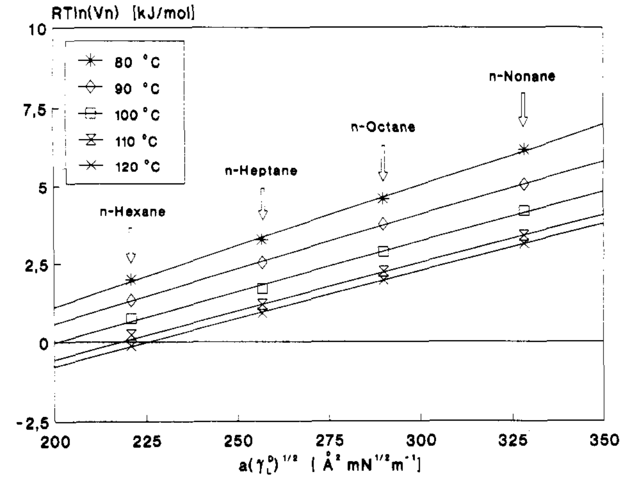

Figure 1. $RT \ln V_N$ versus $a(\gamma_L^D)^{1/2}$ plot for the adsorption of n-alkanes on polycarbonate.

authors. We note that DN is free of dispersion force effects.[34]

This approach, based on the Gutmann two-parameter model but using DN and AN* values, seems of particular value because (i) it takes into account the amphoteric character of most molecules,[34] (ii) it evaluates both the basicity (DN) and the acidity (AN*) of solutes from enthalpy changes with the reference acid SbCl$_5$ or the reference base Et$_3$PO, and (iii) DN and AN* values are available for solutes covering a broad range of acid–base characteristics. This convention will be used throughout the present work.

Experimental Section

1. **Materials.** The polymer used in this work was Lexan 140 polycarbonate, supplied by General Electric Co. For IGC work, the polymer was coated onto Chromosorb G, AW/DMCS, 60/80-mesh support from 2% solutions in chloroform. The weight of supported PC was found to be 7% of the total solids weight. A previously degreased and dried stainless steel column, 0.5 m in length and 0.6 cm in diameter, was packed with 5.6 g of the coated support and used in all experiments discussed below. The mobile-phase adsorbates involved in this work were n-hexane (n-C6), n-heptane (n-C7), n-octane (n-C8), n-nonane (n-C9), diethyl ether, tetrahydrofuran (THF), ethyl acetate (EtAc), acetone, dichloromethane (DCM), and chloroform. All were analytic-grade materials, used as received.

2. **IGC Procedures.** IGC measurements were made with a Varian 3400 gas chromatograph, equipped with both thermal conductivity and flame ionization detectors. The carrier gas was helium. The flow rate was 30 mL/min, corrected for pressure drop along the column and for temperature variations between the column and a soap bubble flowmeter.

All IGC measurements were at temperatures between 80 and 120 °C, that is, below the T_g of PC. Hence, surface adsorption was the dominant mechanism, and absorption of probe molecules into the bulk of the deposited polymer could be neglected. Extremely small quantities of vapor were injected into the column from 1-μL Hamilton syringes. Retention signals were generally found to be symmetrical, although n-alkanes produced relatively broad peaks. These signals were found to be independent of the vapor quantity injected. Retention times were obtained from differences between peak maxima and both air and methane markers. At least five separate determinations were used in averaging the net retention volume, data reproducibility throughout being better than 5%.

Results and Discussion

An initial presentation of results tests the validity of eq 6. The result of this procedure is shown in Figure 1. The excellent linearity of each isotherm confirms the applicability of this expression to polymeric stationary phases.

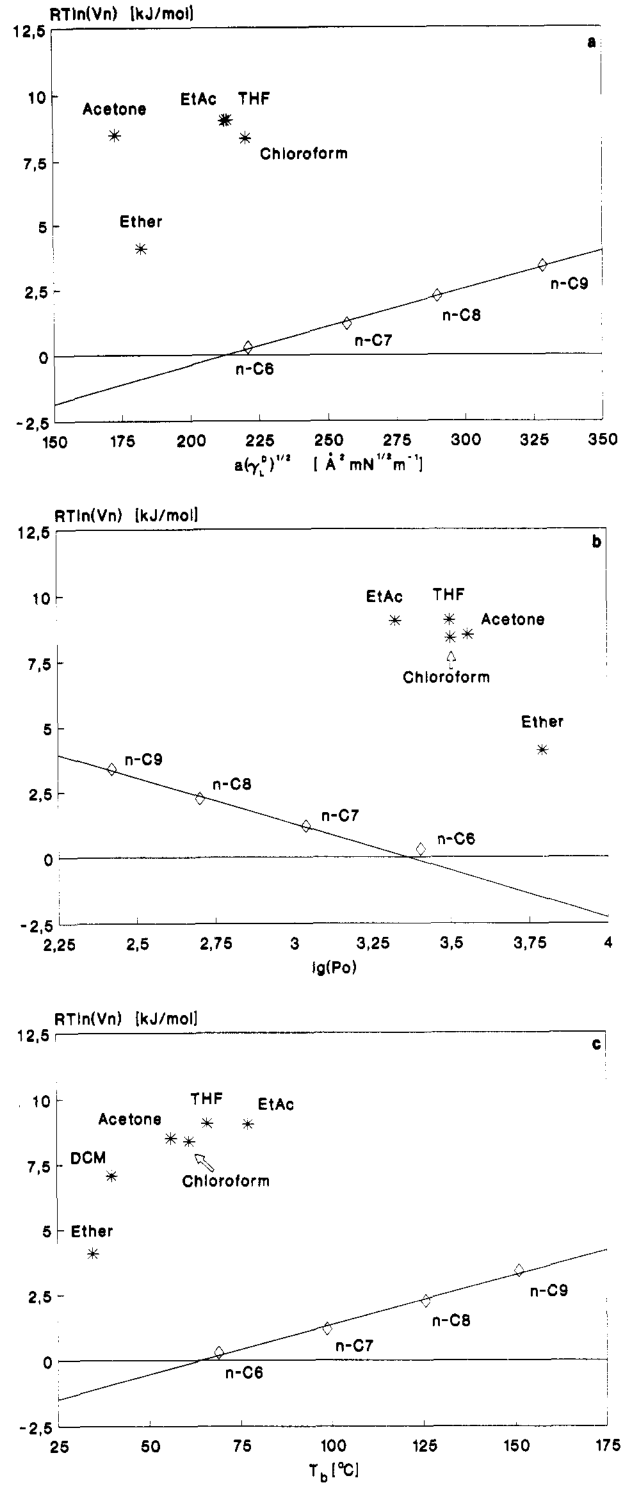

Figure 2. Determination of specific contributions to the free energy of adsorption from IGC data by plotting $RT \ln V_N$ versus (a) $a(\gamma_L^D)^{1/2}$ (method I), (b) $\log P_0$ (method II), and (c) T_b (method III).

From the slope of these lines, γ_S^D may be calculated. The value obtained was 14.2 mJ/m^2 at 80 °C. This is significantly lower than expected, in part due to the elevated temperature of the determination. Another possible reason may lie in the chosen values of the molecular area. Our choice did not take into account possible perturbations of the adsorbing molecule by the solid in question, an event which would maintain the linearity of relationships in Figure 1 but would change their slope.

Following earlier discussions, it is of interest to determine specific interaction contributions to net retention volumes from the three variations of the abscissa definition. This is done in parts a–c of Figure 2, which illustrate the

Table I
Specific Components ΔG_A^{sp} of the Free Energy of Adsorption of Solutes on Polycarbonate Lexan at 110 °C

solute	ΔG_A^{sp}/(kJ mol^{-1}) method I	method II	method III
diethyl ether	5.0	5.6	5.2
acetone	9.7	9.2	8.8
chloroform ($CHCl_3$)	8.1	8.8	8.5
tetrahydrofuran (THF)	9.0	9.5	9.0
ethyl acetate (EtAc)	9.1	8.8	8.5

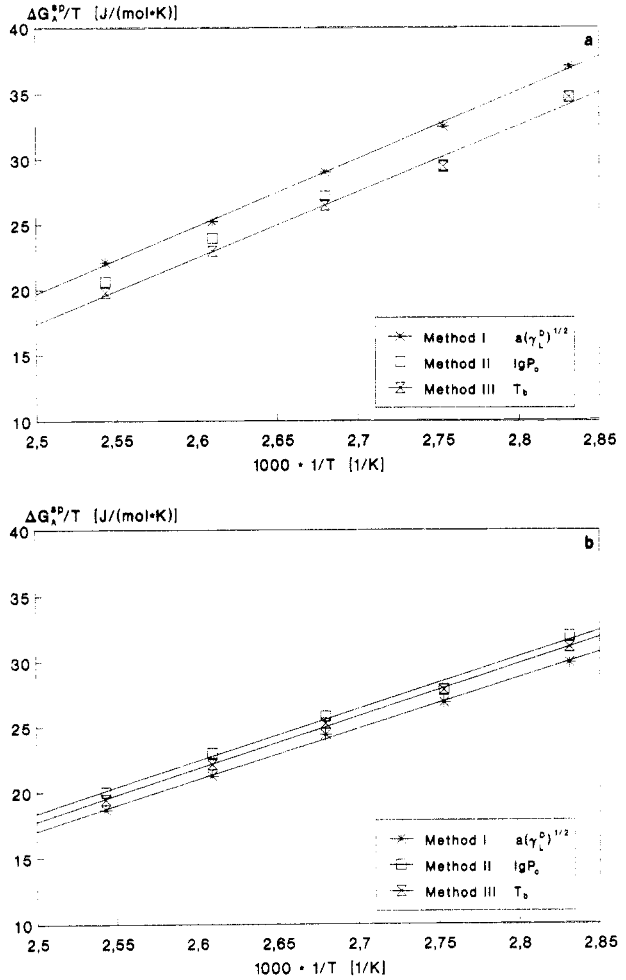

Figure 3. Evaluation of specific enthalpies of adsorption according to eq 12 by plotting $\Delta G_A^{sp}/T$ versus $1/T$: (a) acetone on polycarbonate; (b) chloroform on polycarbonate.

point for data at 110 °C. The differences between the measured retention volumes and the reference line given by the n-alkanes are used to compute the specific interaction contributions, ΔG_A^{sp}, to the free energy of adsorption. The pertinent data are listed in Table I.

Methods I–III (see above) lead to ΔG_A^{sp} values which vary somewhat with the choice of adsorbate but which are essentially equal for any given probe.

Arguably more relevant are the values of the specific contributions ΔH_A^{sp} to the enthalpy of adsorption. These have been calculated from

$$\Delta G_A^{sp} = \Delta H_A^{sp} - T\delta S_A^{sp} \tag{12}$$

where ΔS_A^{sp} is the specific contribution to the change in entropy due to adsorption per mole of adsorbate. Thus the slope of plots of $\Delta G_A^{sp}/T$ vs $1/T$ is equated to ΔH_A^{sp}. The procedure is shown for acetone and chloroform in parts a and b of Figure 3. All values of ΔH_A^{sp} are summarized in Table II.

Table II
Specific Components ΔH_A^{sp} of the Enthalpy of Adsorption of Solutes on Polycarbonate Lexan Determined by Use of Equation 12

solute	$-\Delta H_A^{sp}$/(kJ mol^{-1}) method I	method II	method III
diethyl ether	48.1	50.0	49.2
acetone	51.7	47.0	50.6
chloroform ($CHCl_3$)	39.2	40.0	40.4
tetrahydrofuran (THF)	46.7	48.4	46.4
ethyl acetate (EtAc)	52.5	52.1	51.0

Table III
Acid–Base Characteristics of Solutes in This Study (According to Riddle–Fowkes[34])

solute	DN/ (kcal/mol)	AN	AN^d	AN*/ (kcal/mol)	DN/AN*
diethyl ether	19.2	3.9	−1.0	1.4	13.7
tetrahydrofuran	20.0	8.0	6.1	0.5	40.0
ethyl acetate	17.1	9.3	4.0	1.5	11.4
acetone	17.0	12.5	3.8	2.5	6.8
dichloromethane	0	20.4	6.9	3.9	0.0
chloroform	0	23.1	6.4	5.4	0.0

These representations show clearly that methods I–III lead to almost equivalent values of ΔH_A^{sp}. Small apparent differences in ΔS_A^{sp} (intercepts of graphs in Figure 3a,b) may be due to experimental uncertainties.

We may conclude that these results do not identify any one method of data representation as being superior to the others. Secondary considerations therefore affect the decision. Ours was to use method III, that of Sawyer,[24,25] for the separation of dispersion and specific interactions because (i) the boiling temperatures of most widely-used solutes are readily available, (ii) the difficulties in determining exact values of the molecular area a and of the dispersion component γ_L^D of the surface free energy for polar solutes are avoided, and (iii) no calculations are needed of vapor pressures over relevant temperature ranges. The donor numbers DN and acceptor numbers AN* of the solutes used in this study are listed in Table III. By inspection of DN and AN* values, we note that the chosen polar solutes exhibit either strong donor character (tetrahydrofuran, diethyl ether, ethyl acetate) or strong acceptor character (chloroform, dichloromethane). As expected, acetone is an amphoteric substance.

By assigning acid and base indexes to the solid polymer adsorbent and DN and AN* to the solute (probe vapor), the acid–base contribution to enthalpy changes, ΔH^{ab}, resulting from the interaction of solute–solvent pairs is stated as

$$-\Delta H^{ab} = K_a DN + K_b AN^* \tag{13}$$

where K_a and K_b characterize the ability of the solid under investigation to accept or to donate electrons. Thus, by assuming that the specific interactions are in fact Lewis acid–base interactions, we have that

$$\Delta H_A^{sp} = \Delta H^{ab} \tag{14}$$

Consequently, ΔH_A^{sp} determined for IGC and the acid–base properties of solutes and the solid adsorbents are related as follows:

$$-\Delta H_A^{sp} = K_a DN + K_b AN^* \tag{15}$$

Plotting $-\Delta H_A^{sp}/AN^*$ vs DN/AN^* should generate a straight line, with K_a and K_b evaluated respectively from its slope and intercept. The relevant plot for the PC is shown in Figure 4; we note that the ΔH_A^{sp} values are expressed in kilocalories per mole units.

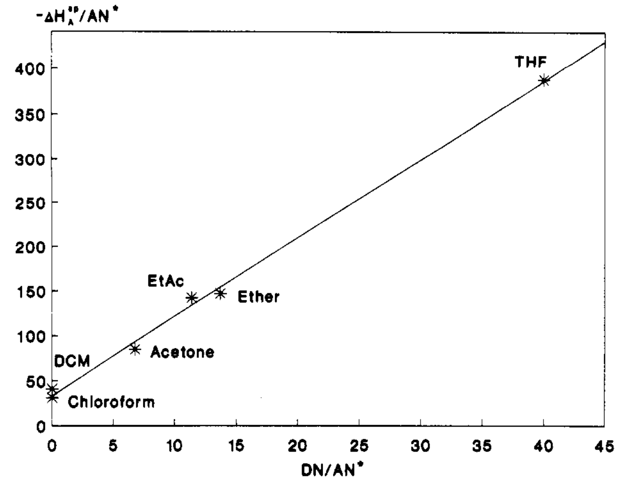

Figure 4. Correlation between specific enthalpies $\Delta H_A{}^{sp}$ of adsorption of the chosen solutes on polycarbonate and the DN and AN* values of these solutes according to eq 15.

The linear relation is excellent, indicating that the Gutmann acid–base concept is applicable to these systems and that the specific interactions referred to may be taken as electron donor–acceptor interactions. Applying eq 15, we obtain values of 8.8 for K_a and 33.2 for K_b. Evidently polycarbonate is amphoteric and able to function as an electron acceptor as well as an electron donor. The latter capacity is dominant, however, so that PC is considered to be predominantly basic. This conclusion is in good agreement with the results of Bolvari and Ward.[13]

Conclusions

In this work we have used the well-established method of inverse gas chromatography to evaluate the acid–base properties of a Lexan polycarbonate. By using *n*-alkanes and polar solutes as adsorbates, the specific contributions $\Delta G_A{}^{sp}$ to the free energy of adsorption were determined from plots of $RT \ln V_N$ versus (I) $a(\gamma_L{}^D)^{1/2}$, (II) logarithms of vapor pressure $\log P_0$, and (III) boiling points T_b of the solutes. After comparing these three methods as means for separating dispersion and specific interactions, further use was made of method III because of its experimental convenience.

Enthalpies of acid–base interaction were determined from the temperature dependence of $\Delta G_A{}^{sp}$. These enthalpies were found to correlate with Gutmann's donor numbers DN and new acceptor numbers AN* introduced by Riddle and Fowkes in units of kilocalories per mole, that is, in the same units as the donor numbers. Consequently, the PC adsorbent is also characterized by means of two parameters describing its acidity (K_a) and basicity (K_b) in consistent units. It was shown that the Lexan polymer, while predominantly basic, retains subordinate acceptor properties and is more accurately described as amphoteric.

References and Notes

(1) Schreiber, H. P.; Lloyd, D. R. In *Inverse Gas Chromatography*; ACS Symposium Series 391; Lloyd, D. R., Ward, T. C., Schreiber, H. P., Eds.; American Chemical Society: Washington, DC, 1989; p 1.
(2) Williams, D. In *Controlled Interphases in Composite Materials*; Ishida, H., Ed.; Elsevier: New York/Amsterdam/London, 1990; p 219.
(3) Fowkes, F. M.; Mostafa, M. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 3.
(4) Fowkes, F. M. *J. Adhes. Sci. Technol.* **1987**, *1*, 7.
(5) Chappell, P. J. C.; Williams, D. R. *J. Colloid Interface Sci.* **1989**, *128*, 450.
(6) Nardin, M.; Balard, H.; Papirer, E. *Carbon* **1990**, *28*, 43.
(7) Tsutsumi, K.; Ohsuga, T. *Colloid Polym. Sci.* **1990**, *268*, 38.
(8) Tiburcio, A. C.; Manson, J. A. *J. Appl. Polym. Sci.* **1991**, *42*, 427.
(9) Briscoe, B. J.; Roach, S.; Williams, D. R. In *Interfacial Phenomena in Composite Materials*; Jones, F., Ed.; Butterworth: Guildford, 1989; p 162.
(10) Boluk, M. Y.; Schreiber, H. P. *Polym. Compos.* **1989**, *10*, 215.
(11) Panzer, U. *Colloids Surf.* **1991**, *57*, 369.
(12) Lavielle, L.; Schultz, J. *Langmuir* **1991**, *7*, 978.
(13) Bolvari, A. E.; Ward, T. C. In *Inverse Gas Chromatography*; ACS Symposium Series 391; Lloyd, D. R., Ward, T. C., Schreiber, H. P., Eds.; American Chemical Society: Washington, DC, 1989; p 217.
(14) Osmont, E.; Schreiber, H. P. In *Inverse Gas Chromatography*; ACS Symposium Series 391; Lloyd, D. R., Ward, T. C., Schreiber, H. P., Eds.; American Chemical Society: Washington, DC, 1989; p 230.
(15) Papirer, E.; Vidal, A.; Balard, H. In *Inverse Gas Chromatography*; ACS Symposium Series 391; Lloyd, D. R., Ward, T. C., Schreiber, H. P., Eds.; American Chemical Society: Washington, DC, 1989; p 248.
(16) De Boer, J. H.; Kruyer, S. *Proc. K. Ned. Akad. Wet.* **1952**, *355*, 451.
(17) Kemball, C.; Rideal, E. K. *Proc. R. Soc. London* **1946**, *A187*, 53.
(18) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*, 40.
(19) Emmett, P. H.; Brunauer, S. *J. Am. Chem. Soc.* **1937**, *59*, 1553.
(20) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.
(21) Schultz, J.; Lavielle, L.; Martin, C. *J. Adhes.* **1987**, *23*, 45.
(22) Saint Flour, C.; Papirer, E. *J. Colloid Interface Sci.* **1983**, *91*, 63.
(23) Papirer, E. In *Composite Interfaces*; Ishida, H., Koenig, J. L., Eds.; North-Holland: New York/Amsterdam/London, 1986; p 203.
(24) Sawyer, D. T.; Brookman, D. J. *Anal. Chem.* **1968**, *40*, 1847.
(25) Brookman, D. J.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 106.
(26) Fowkes, F. M. *Org. Coat. Plast. Chem.* **1979**, *40*, 13.
(27) Fowkes, F. M. In *Physicochemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum Press: New York/London, 1983; Vol. 2, p 583.
(28) Drago, R. S.; Wayland, B. *J. Am. Chem. Soc.* **1965**, *87*, 3571.
(29) Drago, R. S.; Parr, L. B.; Chamberlain, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 3203.
(30) Gutmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.
(31) Gutmann, V.; Steininger, A.; Wychera, E. *Monatsh. Chem.* **1966**, *97*, 460.
(32) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235.
(33) Deng, Z.; Schreiber, H. P. In *Contemporary Topics in Polymer Science*; Culbertson, B. M., Ed.; Plenum Press: New York/London, 1989; Vol. 6, p 385.
(34) Riddle, F. L.; Fowkes, F. M. *J. Am. Chem. Soc.* **1990**, *112*, 3259.